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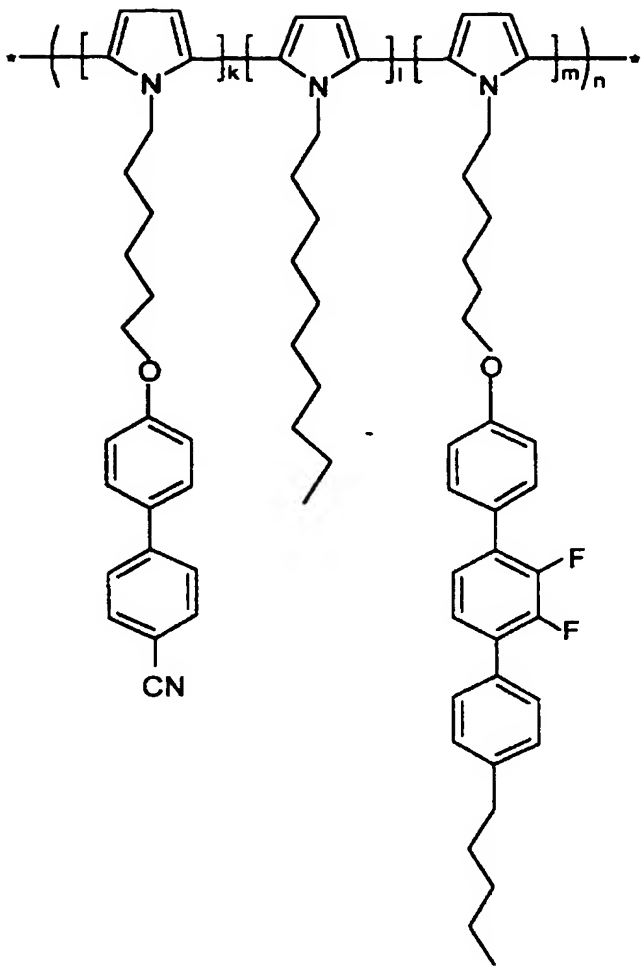
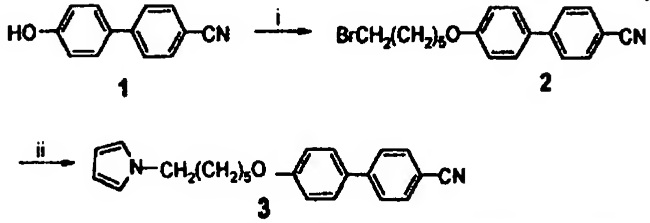
Figure 1.

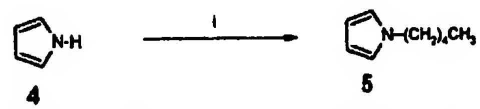


Where:
$1 \leq k \leq 200$
$0 \leq l \leq 50$
$1 \leq m \leq 200$
$1 \leq n \leq 10$

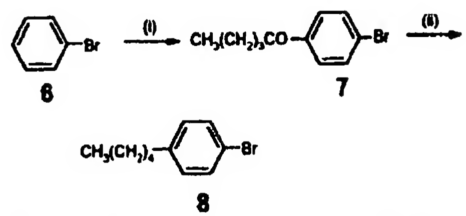
Reaction Schemes



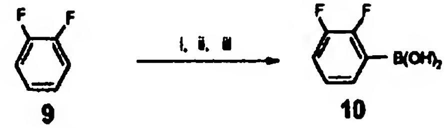
Scheme 1 *Reagents* ; i, $Br(CH_2)_6Br$, K_2CO_3,cyclohexanone; ii, pyrrole $KOC(CH_3)_3$, 18-crown-6.



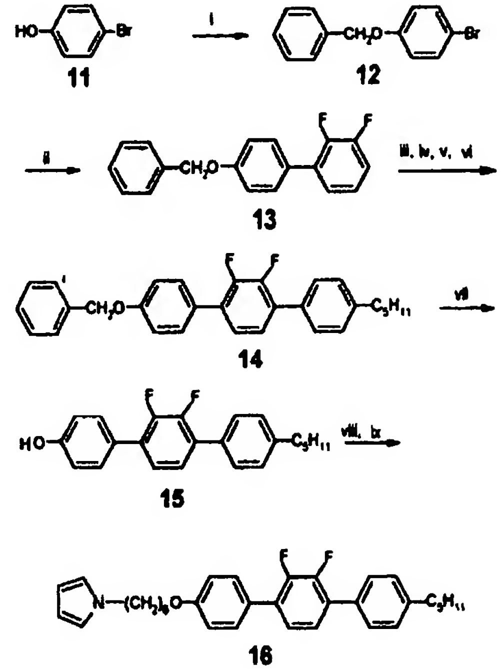
Scheme 2 *Reagents;* i, $CH_3(CH_2)_4Br$. $KOC(CH_3)_3$. 18-crown-6.



Scheme 3 *Reagents;* i, C_4H_9COCl, $AlCl_3$; ii, hydrazine hydrate, KOH.



Scheme 4 *Reagents;* i, n-BuLi, THF; ii, $(MeO)_3B$, THF; iii, dil HCl



Scheme 5 *Reagents;* i, Benzyl bromide, K_2CO_3, cyclohexanone; ii, compound 10, $Pd(PPh_3)_4$, Na_2CO_3, $CH_3OCH_2CH_2OCH_3$, H_2O; iii, n-BuLi, THF; iv, $(MeO)_3B$, THF; v, dil HCl; vi, compound 8, $Pd(PPh_3)_4$, Na_2CO_3, $CH_3OCH_2CH_2OCH_3$, H_2O; vii, Pd on C, H_2; viii, $Br(CH_2)_6Br$, K_2CO_3,cyclohexanone; ix, pyrrole, $KOC(CH_3)_4$, 18-crown-6.

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CONDUCTING POLYMERS WITH SWITCHABLE MAGNETIC/ELECTRONIC PROPERTIES

This invention relates to a range of copolymers which exhibit strong switching of their electrical and optical properties under the influence of external stimuli. The general structural feature of these materials is a conjugated π polymer backbone which may be semiconducting or conducting (i.e. one with an energy–gap between zero and about three electron volts in its unsubstituted form). The backbone is substituted with pendant mesogens and spacer groups of various lengths in either sequential block arrangements or alternating copolymer arrangements. (A typical example is shown in Figure 1.)

The polymer backbone may advantageously comprise units of pyrrole, thiophene, aniline or carbazole. These may be substituted in some or all available positions with suitable flexible spacers, preferably an *n*-alkyl or *n*-alkyloxy chain of length between one and eighteen carbon atoms which may or may not be terminally substituted with a mesogenic moiety. Preferred repeat units are 3- or 3,4-substituted-2,5-pyrrole- or thiophenediyl, N-substituted 2,5-pyrrolediyl, 2- or 2,5-substituted anilinediyl or N-substituted 3,6-carbazolediyl. The mesogenic moieties are grouped in sequences of positive or negative dielectric anisotropies or may optionally have a dielectric anisotropy that is electric field frequency dependent.

The invention was based on research into new, stable liquid crystal conducting polymers which have externally variable conduction arising from the application of an external electric or magnetic field when the polymer is in a liquid crystal phase. This results from the tendency for mesogenic side group molecules with positive dielectric

anisotropy to align parallel to the applied electric field, and molecules with a negative dielectric anisotropy to align perpendicular to the applied field. Molecules with a frequency dependent dielectric anisotropy will have a molecular alignment which is dependent on the frequency of the electric field to which they are exposed. These various alignments will apply torque to the polymer backbone and interrupt the conjugation of the polymer producing changes in electronic conduction and electrical properties.

According to the invention, we provide organic copolymers having a conjugated π backbone, substituted with pendant mesogens and flexible spacer groups of various lengths in either sequential block or alternating copolymer arrangements, in which the mesogenic moieties are either (i) grouped in sequences comprising moieties having a positive dielectric anisotropy and moieties having a negative dielectric anisotropy, or (ii) are such that they have dielectric anisotropy that is electric field dependent such that they align either parallel or perpendicular to the applied electric field depending on its frequency.

It has been found that these polymer systems have externally variable conduction when exposed to an external electric or magnetic field in their liquid crystal state. It has been found necessary in many cases to convert the polymer into the liquid crystal phase either by conventional bulk thermotropic methods or by the application of a focussed laser beam while simultaneously applying an electric or magnetic field. In the prior art *[British Patent Applications GB 2304723 and GB 2318119]* liquid crystal conducting polymers have been used to generate externally variable conduction. Such systems should be distinguished from that in the present invention which in addition to

developing self ordering properties arising from the liquid crystal phase allows the order and orientation in the liquid crystal and resulting polymer effective conjugation to be electrically or magnetically driven by external fields. This results in much greater range of external variability in the conduction and switching properties of the polymer.

The potency of the electric or magnetic field variable alignment will depend on the symmetry and regularity of the aromatic or heteroaromatic repeating units in the polymer backbone. Thus, for a polymer in which the mesogenic group is attached to a repeating unit which is "reversible" (such as N-substituted poly(2,5-pyrrolediyl) or polycarbazole which have a plane of symmetry) the variability is readily obtainable. However, if for example the mesogenic group is attached to the 3-position of a thiophene monomer, the maximum beneficial effect of the present invention will only be obtained if the resulting polymer has been formed by a regiospecific polymerisation method. Such methods are well known in the prior art [e.g. TA Chen and RD Rieke, *J. Amer. Chem. Soc.*, 114, (1992), 10087.] and need not be detailed herein.

Synthesis Example 1

An example of a suitable synthetic route for the preparation of the pyrrole monomers is given in the following **Schemes 1-5** which are subsequently polymerised, or oligomerised and subsequently polymerised in appropriate ratios.

All starting materials are known or prepared in analogy to known starting materials.

Other routes for the preparation of the polypyrroles and other polymers and monomers are apparent to the skilled worker. All these steps and the corresponding reaction conditions are known to the skilled worker.

Fields of Application

These materials would have potential applications in the production of polymer films of controllable conductivity, or as antistatic coatings, or as circuit boards on which the conducting tracks have been produced by a combination of laser and applied electric fields, or in a new generation of non-silicon based molecular microprocessors.

CLAIMS

1. Organic copolymers having a conjugated π backbone, substituted with pendant mesogens and flexible spacer groups of various lengths in either sequential block or alternating copolymer arrangements, in which the mesogenic moieties are either (i) grouped in sequences comprising moieties having a positive dielectric anisotropy and moieties having a negative dielectric anisotropy, or (ii) are such that they have dielectric anisotropy that is electric field dependent such that they align either parallel or perpendicular to the applied electric field depending on its frequency.

2. Copolymers as claimed in Claim 1 which have externally variable conduction and optical properties arising from the application of an external electric or magnetic field when the polymer is in a liquid crystal phase.

3. Copolymers as claimed in Claim 1 which have externally variable conduction and optical properties arising from the application of a focused laser beam while simultaneously applying an electric or magnetic field.

4. Copolymers as claimed in Claims 1, 2 or 3 which have pendant mesogenic side groups with positive dielectric anisotropy that align parallel to an applied electric field and mesogenic side groups with a negative dielectric anisotropy that align perpendicular to an applied electric field.

5. Copolymers as claimed in any previous claim, wherein the various alignments of the pendant mesogenic side groups apply torque to the polymer backbone and interrupt the conjugation of the polymer.

6. Copolymers as claimed in any previous claim, wherein the various alignments of the pendant mesogenic side groups increase the conjugation of the polymer.